Evolution of structure and properties of PAN precursors during their conversion to carbon fibers

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Abstract

The formation and evolution of structure, and the changes of properties during the preoxidation, precarbonization, and carbonization of different PAN precursors were studied by the combination of DSC, FT-IR, SEM and some traditional measurements, such as density and mechanical properties of various fibers. The exothermic regime of polyacrylonitrile-based precursors made of acrylonitrile/itaconic acid (AN/IA) copolymers or acrylonitrile/acrylamide (AN/AM) copolymers is much broader and the cyclization reaction starts at lower temperature, compared to that of PAN homopolymer precursors, but AM appears to be more effective in separating the exothermic reactions corresponding to preoxidation stages in DSC curves as compared to IA. If AN/IA (97.5/2.5 w/w) precursors and AN/AM (97.5/2.5 w/w) precursors are designated as P1 and P2, respectively, the AM-containing commercial precursors (P3) are thermally more stable than the P2 ones, and the density of P3 is higher than that of P1 or P2. This may result from the difference of aggregation morphology among the original precursors, since it is dense for P3 precursors, whereas P2 and P1 precursors have some voids. The tensile strength of resultant carbon fibers from P3 precursors was better than that of carbon fibers from P2 or P1 after identical conditions of preoxidation are employed.
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1. Introduction

Carbon fibers can be produced from a variety of precursors, such as polyacrylonitrile (PAN), mesophase pitch, rayon, etc., among which PAN-based carbon fibers are the preferred reinforcement for structural composites with the result of their excellent specific strength and stiffness combined with their light weight as well as lower cost. In order to meet expanded use in some high-tech sectors, many novel approaches, such as dry-wet spinning [1], steam drawing [2], increasing the molecular weight of precursors polymer [3], modifying the precursors prior to stabilization [4], etc., have been performed to increase the tensile strength of PAN-based carbon fibers. Now it has been popularly accepted that the quality of the high performance carbon fibers depends mainly on the composition and quality of the precursor fibers. However, the physical and chemical structural transformations that take place during heat treatments are extremely complicated. However, it is difficult to predict how to effectively improve the performances of the resultant carbon fibers, and it is not fully clear which one comonomer is the optimum selection and which one precursor index has the most influence on their structure and properties because of commercial secrets or other reasons. One way to address these issues is to take different PAN precursors and comparatively study their different evolution of structure features and properties of PAN precursor fibers during the thermal stabilization and carbonization process. In this study, some factors limiting the mechanical properties of carbon fibers are investigated, with the aim of generating guidelines to improve the quality of the resultant carbon fibers.

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2. Experimental

2.1. Materials

Different PAN precursors (named as P0, P1, P2 and P3, respectively) were selected in this study. For wet spinning precursor P1 fibers, a 20 wt.% solution was prepared in dimethylsulfoxide (DMSO) by using a copolymer of acrylonitrile/itaconic acid (AN/IA 97.5/2.5 w/w) with average molecular weight of 150 000 g mol^{-1}. For precursor P2 fibers, which were wet-spun from a 22 wt.% solution in DMSO of a copolymer of acrylonitrile/acrylamide (AN/AM 97.5/2.5 w/w) with average molecular weight of 110 000 g mol^{-1}. In comparison, a PAN precursor, designated as P0, was also wet-spun from a 22 wt.% solution in DMSO using a homopolymer of acrylonitrile with average molecular weight of ca. 120 000 g mol^{-1}. The precursor P3 fibers, however, were supplied by Mitsubishi Rayon (Japan). All these mentioned precursor fibers contain 3000 filaments each single tow, their quality indices are listed in Table 1.

2.2. Preoxidation and carbonization

A self-designed pilot carbon fibers production line, which is composed of two oxidizing furnaces and two horizontal furnaces, respectively, is used for the preoxidation and closely linked carbonization of PAN precursors. Each furnace has some separated temperature zones. The whole temperature zones were programmed as the follows: 125–192–203–214–231–243–253–268–283–428–603–803–1003–1350 °C. The first oxidation oven has four different temperature zones, and the second oxidation oven has five different temperature zones. In the first two hot-air circulation preoxidation furnaces, a precursor fiber was thermal stabilized in a purified air atmosphere at 125–283 °C under a 10% stretching ratio, the total preoxidation time was about 50 min before forming a preoxidized fiber. Subsequently, this preoxidized fiber was subjected to a pre-carbonization in an atmosphere of pure nitrogen from 428 to 803 °C with a fixed length, then a carbonization also in oxygen-free nitrogen from 1003 to 1350 °C under a 1% shrinkage to get carbon fibers. So the processing speed of about 50 m/h was maintained in all the parallel experiments.

2.3. Measurements

Density of various fibers was obtained at 25 °C by the use of density gradient column method. Two columns were used: one comprising a mixture of *n*-heptane and carbon tetrachloride with a gradient from 1.00 to 1.60 g/cm^3, and the other comprising carbon tetrachloride and 1,3-dibromopropane with a gradient from 1.55 to 1.90 g/cm^3. For a given fiber sample, dissolved in DMSO at 80 °C for 6 h, then filtered, washed using water then washed again with acetone, dried in vacuum oven to a constant weight. The weight of insoluble residues was divided by the total weight of its before dissolving to obtain the solubility. The exothermic reaction of PAN precursors was determined by the use of differential scanning calorimetry (DSC) which was carried out on a DSC-7 module of a Perkin-Elmer Delta series thermal analyzer. These DSC studies were performed at a heating rate of 10 °C in nitrogen atmosphere with sample weights of about 2.5 mg. A Netzsch DSC 404 was also used to obtain the high-temperature DSC curves of the P2 or P3 precursors, and the fibers from original P2 after preoxidation or precarbonization investigated in argon with a heating rate of 20 °C/min in the range of 25–1400 °C using about 9-mg samples. Fourier transform infrared (FT-IR) measurements were made by loading samples on KBr disks (0.5 mg sample with 200 mg KBr) for the specimens which were selected from fibers after different heat temperatures, by the use of a Nicolet750 Magna-IR. The titre (the linear density of fibers, its unit has denier, tex, and dtex, e.g., 1 dtex equals to the grams of a 10 000-m long filament) of a filament was measured by a XD-1 fiber fineness machine, and mechanical properties of PAN precursors, preoxidized fibers and carbon fibers were measured by a XQ-1 tensile-testing machine (both XD-1 and XQ-1 were made in Donghua University, Shanghai, China) at a crosshead speed of 0.5 mm/min with a testing length of 20 mm and load cell of 10 g. In each case, at least 30 sample filaments were tested, and the average of 30 filaments was taken for each experiment.

Table 1
Some quality indices of selected PAN precursors

Precursor	Titre (dtex)	Density (g cm^{-3})	Tensile strength (MPa)	Elongation (%)	Crystallinity (%)	Composition (wt.%)
P1	1.14	1.07	633.6	10.8	52	AN/IA(97.5/2.5)
P2	1.63	1.08	533.5	11.7	55	AN/AM(97.5/2.5)
P3	1.24	1.17	578.5	10.6	87	AM-containing[a]

[a] Deduced from the result of this study.

3. Results and discussion

3.1. Effect of comonomers

The effect of copolymer composition has been studied by using different comonomers for P1 and P2, which allow comparison of cyclization data for different precursors as long as the reaction environment and temperature remain the same. It has been clearly recognized that the cyclization of PAN homopolymer initiates through a radical mechanism [5] which is faster than the cyclization of AN copolymers with an ionic mechanism [5], so some comonomers, such as IA, MA, AM, etc., have been copolymerized with AN in order that the highly exothermic cyclization could be slowed which would avoid to some extent fusion and breaking of fibers owing to overheating due to the sharply exothermic reaction. But different types of comonomers have notably different effects on the exothermic patterns of PAN precursors. These can be seen in Fig. 1. For comparison, the DSC exothermic curve of PAN homopolymer precursors (named as P0) is also illustrated in Fig. 1a. Fig. 1 also shows the DSC curves of the different PAN precursors tested. The

exothermic regime of both IA-containing and AM-containing PAN precursors is much broader and the cyclization reaction starts at lower temperature for P1 and P2 at 193.8 and 202.9 °C, respectively, compared to that of PAN homopolymer precursors (P0) at 233.1 °C. It has also been found that with the increase of content of not only IA but also AM in the PAN precursors, the initiation temperature of cyclization reaction decreases, so the exothermic regime becomes broader and broader. Although it is useful to alleviate the abrupt exothermic reaction rate, more structure flaws will be caused in the resultant carbon fibers and will reduce their mechanical properties, which is a defect for forming preferred sheet-like graphite structure in the process of preoxidation and carbonization. As a result, a lower and optimal amount of comonomers [6] should be used for increasing the quality of the resultant carbon fibers.

An interesting discovery is that both P2 and P3 have double separated DSC peaks, which makes us ask whether is the cause of AM, and whether P3 contains AM, as does P2. However, the difference of DSC curves between P2 and P3 is that P2 has a lower starting exothermal reaction temperature and a wider DSC exothermal peak from the
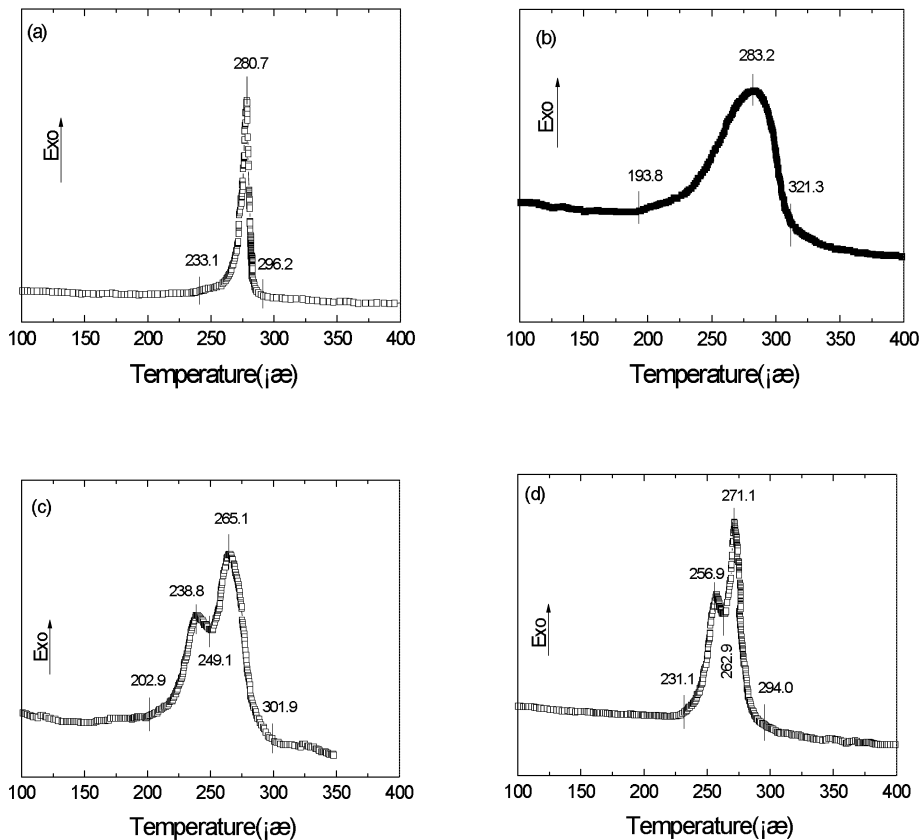

Fig. 1. The DSC curves of (a) P0, (b) P1, (c) P2 and (d) P3 precursors.

start at 202.9 °C to the end at 301.9 °C with two peak values at 238.8 and 265.1 °C, respectively, compared to P3 in the range of 231.1–294.0 °C with two peak values at 256.9 and 271.1 °C, respectively. Therefore, assuming that their comonomer contents and distributions are similar, and even the presence of a little of other comonomer, for example, methyl acrylate, in P3, the content of comonomers in P3 may be less than that in P2.

For IA-containing P1 precursor, there is only one exothermic peak from 193.8 to 321.3 °C with a single peak value at 283.2 °C, but for AM-containing P2, there are two separated peaks, which is similar to the exothermic peak of the commercial one (P3) from Japan. Fig. 2 is the typical FT-IR spectra of three different PAN precursors. The vibrations characteristic of PAN structure are those of CN nitrile group at ca. 2243–2241 cm^{-1}, and the bands in the regions 2931–2870, 1460–1450, 1380–1350, and 1270–1220 cm^{-1} are assigned to the aliphatic CH group vibrations of different modes in CH, CH$_2$, and CH$_3$ [7]. The strong band at 1732 cm^{-1} as shown in Fig. 2a is presented in the P1 PAN precursors, and is attributed to the C=O stretching due to the presence of ester or acid. For AM-containing P2 PAN precursors, as has been shown in Fig. 2b, a characteristic absorbance peak in 1684 cm^{-1} is displayed due to amide group, which corresponds to the peak at 1685 cm^{-1} for the P3 precursor. This can further illustrate our previous deduction that P3 is an AM-containing precursor. In the end, P3 precursors are AM-containing ones which can be deduced according to the following three points: (1) a two separated DSC peak similar to P2; (2) both of P2 and P3 have amide group by the measurement of FT-IR; (3) some public examples in the patents of Mitsubishi Rayon [2,8]. But, these three conclusions are highly speculative. In addition, a shoulder-like appearance at 2191 cm^{-1} near the characteristic absorption for CN (at 2243 cm^{-1}) in P2 precursors, as the arrow indicated in Fig. 2b, may be attributed to the presence of enaminonitrile as a molecular defect formed during polymerization which should be avoided, as has
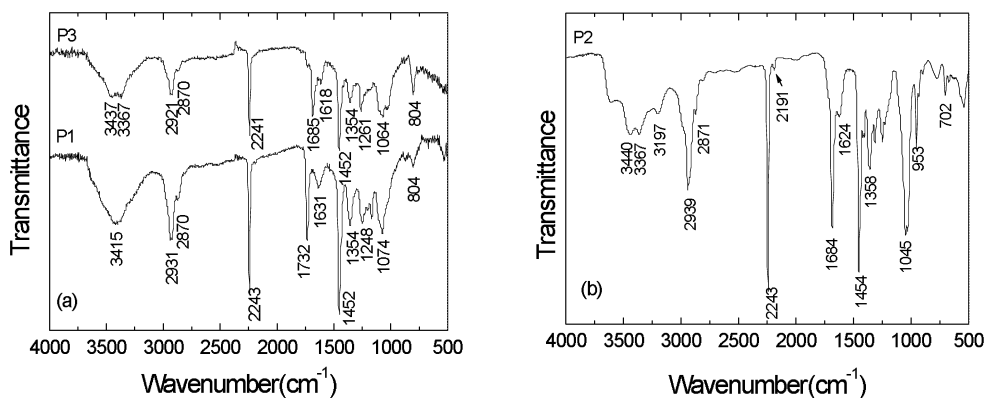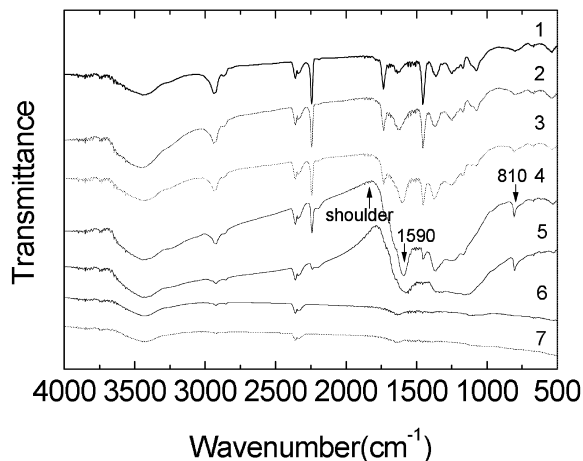

Fig. 3. The FT-IR spectra of P2 precursors after different heat treatment temperature at (1) 125 °C, (2) 214 °C, (3) 231 °C, (4) 253 °C, and (5) 283 °C in air, and (6) 1003 °C and (7) 1350 °C in N$_2$.

been reported by Bajaj et al. [7] and by Gupta et al. [5]. This appearance may also be assigned to the formation of amino-substituted unstaturated nitrile [9] and iminonitriles [10] as a result of partial cyclization or thermal degradation. Certainly, there are other subtle differences between the FT-IR spectra of samples P2 and P3, for example, a shift of some similar bands, which could be attributed to some differences of contents, compositions and distributions between P2 and P3.

3.2. Structural changes

The FT-IR spectra were measured at several points following different heat treatment temperature for P2 and P3. The data were plotted in Figs. 3 and 4 to get information for the structural changes related to the thermal history of the process of preoxidation and carboni-

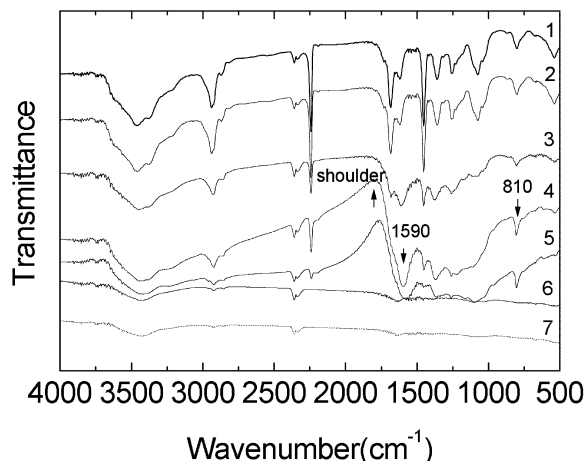Fig. 2. The FT-IR spectra of (a) P1 and P3, and (b) P2 PAN precursors.

Fig. 4. The FT-IR spectra of P3 precursors after different heat treatment temperature at (1) 125 °C, (2) 214 °C, (3) 231 °C, (4) 253 °C and (5) 283 °C in air, and (6)1003 °C and (7) 1350 °C in N$_2$.

zation. The most prominent structural changes were the decrease in the intensities of the 2243–2241 cm^{-1}, attributed to C≡N band, and the decrease of those for aliphatic C–H ones and the decrease of the 1684 or 1685 cm^{-1} amide band for P2 and P3 precursors, respectively, concomitant with the advent and increase of a shoulder-like peak in 1700 cm^{-1} (due to cyclic C=O), the band at 1590 cm^{-1} (due to C=N,C=C,N–H mixed), and the band in 810 cm^{-1} (due to C=C–H) [11]. These spectroscopic results have shown that some chemical processes occurred in the stages of preoxidation. Firstly, reaction of nitriles results in conjugated C=N containing structures which result from intramolecular cyclization or intermolecular crosslinking. Secondly, the generation of conjugated C=C structures results from dehydrogenation or from imine-enamine tautomerization and subsequent isomerization [12]. Thirdly, oxidation gives rise to carbonyl groups. It has also been noted that an unwanted peak at ca. 2330 cm^{-1} is present because of the effect of CO$_2$ in some instrumental conditions.

From the spectral changes, it was also shown that the fibers P2 started cyclization at a lower temperature of compared to P3. In the process of preoxidation, the color of fibers P2 also became yellow at a lower temperature and P3 started to become from white to yellow at a higher temperature. These were in agreement with DSC analysis results, as demonstrated in Fig. 1. As a result, the P3 precursors were thermally more stable than the P2 ones. Although FT-IR showed direct evidence of the changes taking place in the chemistry of preoxidized fibers, once carbonized, not much structural information is available on the carbon fibers due mainly to the difficulty to record a good quality spectrum with conventional techniques owing

to the highly absorbing nature of black carbon fibers samples.

3.3. Changes in precursor density and solubility

The variation of densities and solubility of PAN precursors after preoxidation and carbonization was shown in Fig. 5. During the preoxidation treatment, PAN precursors underwent a series of physical and chemical changes which transformed the original linear polymer structure to a partially cyclized ladder structure, as was demonstrated in Fig. 3 and Fig. 4. The results make the abrupt decrease, especially at the range of 200–280 °C, of solubility of soluble PAN precursors. These become insoluble in DMSO at 80 °C after heat treatment at 283 °C, which is an indication of the extent of preoxidation reaction.

The increase of density in the beginning induction period is very gradual, when PAN precursors mainly undergo physical transformation, e.g., the morphological structure rearrangements. High and adequate stretching is usually imposed in this period in the preoxidation process so as to induce additional orientation and order in the fibers. For any one of P1, P2 and P3 precursors, as a result of consolidation and densification occurring within the fibers, the density increases rapidly in the range of 210–285 °C in air, then increases monotonously to an extreme value, then after the maximum there is a slight drop because of the conversion of open pores to closed pores [13] when temperature rises over 1000 °C.

Comparing the data on the density changes of different P1, P2 and P3 precursors after heat treatment in Fig. 5, it can be observed that the density of P3 is higher than that of P1 or P2. This may be result from the difference of aggregation morphology between their original precursors, as have been listed in Table 1. The original P3 precursors have the highest tensile strength and elongation possibly as
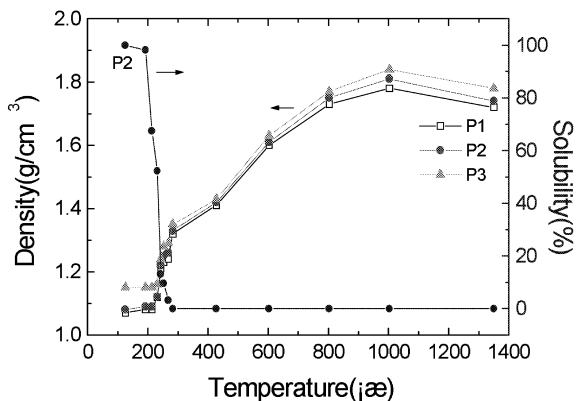

Fig. 5. The changes of density and solubility versus heat treatment temperature for PAN precursors (The preoxidation from 125 to 283 °C is in air, the pre-carbonization and carbonization from 428 to 1350 °C are in N$_2$.)
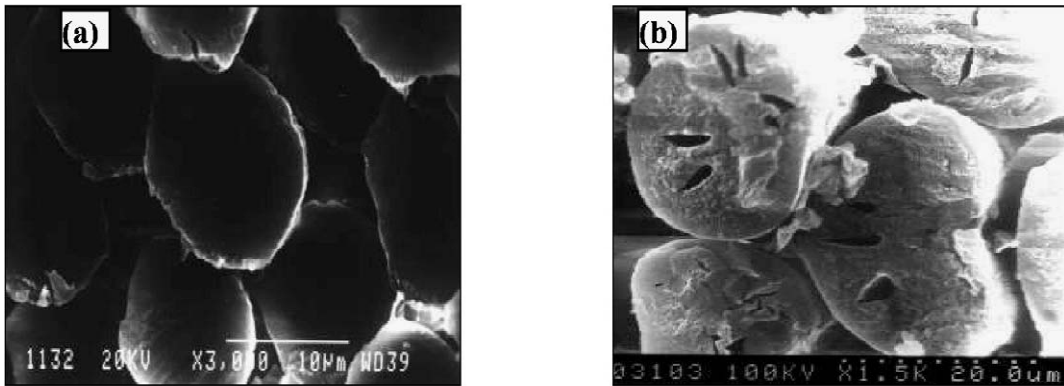
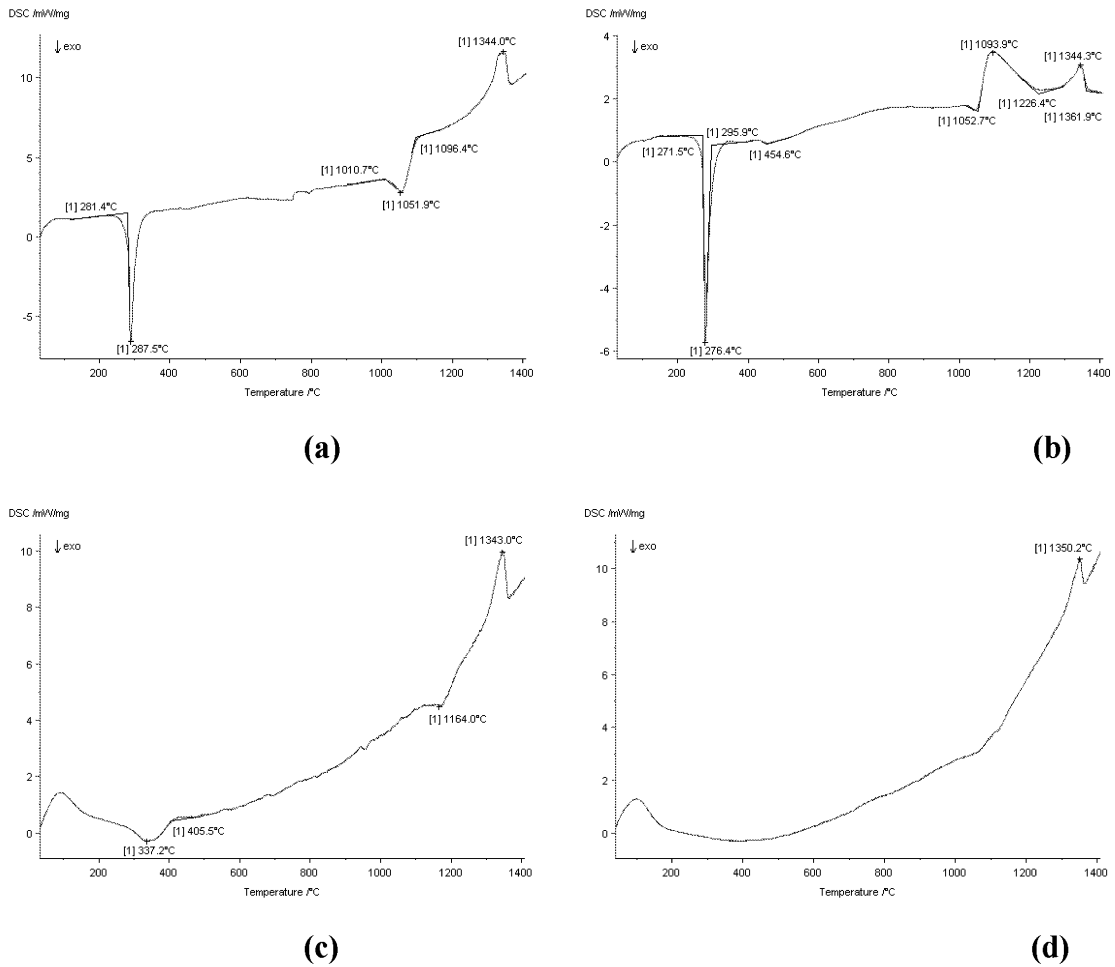Fig. 6. The crosswise SEM photos of (a) P3 and (b) P2 precursors.

Fig. 7. The DSC curves in argon of (a) P2 precursors, (b) P3 precursors, (c) preoxidized fibers from P2 after 283 °C, (d) precarbonized fibers from P2 after 803 °C.

a result of their higher density and higher crystallinity. The cross-sectional SEM photographs of P3 and P2 are illustrated in Fig. 6. It can be clearly seen that it is dense for P3 precursors, whereas P2 precursors have some voids arising from coagulation process of spinning which cause a decreased density. Furthermore, the strength, modulus and elongation at break of fibers depend largely on the number and size of present voids which have substantial influence on the development of the structure, through the whole process from original precursors to resultant carbon fibers.

3.4. Changes in precursor thermal properties

The DSC curves obtained upon heating the P2 or P3 precursors, and the fibers from original P2 after preoxidation or precarbonization investigated in argon with a heating rate of 20 °C/min in the range of 25–1400 °C are given in Fig. 7. When the PAN precursors are preoxidized in air, more functional groups (e.g., C=O) form as a result of the incorporation of oxygen and penetration from the surface to inner part of the fibers with increasing temperature. This will improve the hygroscopicity of preoxidized and/or precarbonized fibers. Therefore, the endotherm at the temperature of 80–120 °C is related to the release of water as shown in Fig. 7c,d. The preoxidized fibers have still an exotherm in the temperature regime of 300–400 °C

with a peak at 337.2 °C, which indicates that the interlinking molecular cyclization of preoxidized fibers is not fully accomplished. Hence, a precarbonization process is required to further perform enough intermolecular cyclization, so the precarbonized fibers do not show the same exothermic reaction as that the corresponding preoxidized fibers from identical original PAN precursors.

In Fig. 7, it can also be seen that there is a common endothermic reaction at ca. 1344–1350 °C for all precursors, preoxidized fibers, and precarbonized fibers. However, there are some differences between the plots of P2 and P3 precursors, as shown in Fig. 7a,b. Only the P3 precursors have a weak exotherm at 454.6 °C, which is not clearly discernible in P2 precursors. P2 precursors have a stronger exothermic reaction at 1051.9 °C compared that of P3 ones at 1052.7 °C. The characteristic difference is that P3 precursors have a strong endotherm at 1093.9 °C which may be an important factor to facilitate dealing with the carbonization process. A possible reason is that this endothermic reaction may alleviate the breakage of a filament due to denitrogenation during the final carbonization stage. This can also be regarded as a new discovery, because DSC curves have been generally reported at temperatures up to –500 °C in the previous public literature. Although the absence of experimental artifacts has been confirmed by running blank analyses for comparison

Table 2
The properties of PAN precursors, preoxidized and carbon fibers with the change of temperature

Temperature (°C)	P1			P2			P3		
	Titre (dex)	Tensile strength (MPa)	Elongation (%)	Titre (dtex)	Tensile strength (MPa)	Elongation (%)	Titre (dtex)	Tensile strength (MPa)	Elongation (%)
25 (Precursors)	1.14	633.6	10.8	1.63	533.5	11.7	1.24	578.5	10.6
125	1.17	633.7	10.8	1.61	533.6	11.7	1.24	578.5	10.6
192	1.13	561.9	10.8	1.59	584.9	12.2	1.24	596.4	11.2
202	1.14	567.8	11.0	1.42	565.5	11.9	1.25	581.3	11.3
214	1.09	544.1	11.4	1.61	413.7	11.6	1.26	682.2	11.8
222	1.09	500.2	10.7	1.60	409.7	12.1	1.26	573.8	11.2
231	1.07	491.6	11.4	1.48	419.0	11.3	1.19	602.9	11.4
240	1.18	431.4	11.6	1.52	379.9	13.3	1.24	484.6	11.6
253	1.11	400.1	12.1	1.46	323.0	13.0	1.24	525.8	11.8
268	1.06	355.7	13.5	1.39	287.7	12.6	1.20	486.1	11.9
277	1.02	342.3	15.7	1.35	247.6	10.7	1.18	410.4	13.0
283 (Preoxidized fibers)	1.06	231.6	13.6	1.39	246.5	12.0	1.18	316.4	11.5
428–603–803–1003	1.01	769.2	0.7	0.83	1189.1	1.2	0.85	1373.0	1.5
1350 (Carbon fibers)	0.87	2557.5	0.5	0.77	3507.1	0.8	0.83	3989.4[a]	1.1

[a] According to a patent [2], the tensile strength of a carbon fiber is in the range of 4040–4850 MPa, but its titre and elongation are not disclosed.

using a special grade of 99.9999 wt.% argon as purge gas, whether some other experimental factors may complicate the high temperature DSC data need to be further studied.

3.5. Evolution of mechanical properties

The change of properties of PAN precursors, preoxidized fibers and carbon fibers with heat treatment temperature was tabulated in Table 2. It was shown that the tensile strength decreased with the increase of temperature in the preoxidizing process. However, once carbonized, the tensile strength of carbon fibers had an abrupt increase and the elongation had an abrupt decrease. Carbon fibers P3 had the best tensile strength, P2 was the better, and the P1 had the lowest tensile strength. In case of directing fibers P1 to pass through the final high carbonizing furnace from 1003 to 1350 °C, it was very difficult to deal with because the fibers tow was broken continually. On the contrary, fibers P3 and P2 were easily passed through the final high carbonizing furnace. In addition, the fact that the tensile strength of carbon fibers P3 was better than that of carbon fibers P2, could be the result of different preparation process of the precursors, such as spinning, drawing, and so on, which cause differences in structure and properties, such as differences in density, morphology, and porosity.

4. Conclusion

In order to obtain high performance PAN-based carbon fibers, the combination of both physical mechanical properties and chemical composition should be optimized. Modifying a given property of a precursor at the expense of other property indexes is not an optimal way to prepare carbon fibers. The following conclusion can be drawn:

(1) It is uncertain that high strength PAN precursors are essential in order to obtain high performance carbon fibers, because the composition and morphology of the precursors also play a very important role in the processes of preoxidation, precarbonization and carbonization.
(2) For AM-containing precursors, AM appears to be more effective in separating the exothermic reactions corresponding to preoxidation stages in DSC curves, compared to IA, for IA-containing precursors.
(3) Except for ideal chemical composition, the optimal PAN precursors should have higher density, higher

and adequate strength, higher crystallinity and preferred morphology with as few voids and flaws as possible.

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